Fabrication of Li_2TiO_3 pebble by studying the effect of binder content and sintering temperature on pellets

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

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In
Ceramic Engineering

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2010- 2011

National Institute of Technology Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"Fabrication of Li_2TiO_3 pebble by studying the effect of binder content and sintering temperature on pellets"** submitted by **Mr. Brijesh Kumar Gupta** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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1. Abstract:

Li_2TiO_3 ceramic is being considered as promising solid breeder materials in tritium breeding blanket of thermonuclear fusion reactors, because of its reasonable lithium atom density, prominent tritium release rate at low temperatures between 200 to 400^oC, its low activation characteristics, low thermal expansion coefficient, high thermal conductivity. From design aspect it has found that blanket made of spherical pebble is advantageous because it impart good features like, easy for making complex shapes blanket, uniform pore network, low sensitivity to irradiation damage and cracking, high average bed density and good purge gas drop.

In this work, Li_2TiO_3 powder was prepared by solid state route. Li_2TiO_3 pellets with three different binder content, i.e. 3%, 5% and 7% PVA, were prepared. Then, the effect of binder content and sintering temperature (three different temperatures 900^0C, 1000^0C, and 1100^0C) on density, thermal expansion and microstructure were investigated. Based on this result, Li_2TiO_3 pebble was fabricated with 3 wt% PVA by extrusion and spheronisation process and after sintering bulk density was measured.

2. Introduction:

Fusion Reactions provide a potential energy source with having unlimited fuel supply. These reactions takes place in Fusion reactor which uses a reaction takes place by fusing Deuterium and Tritium. (Tritium is an isotope of Hydrogen which contains one proton and two neutrons.) The reaction proceeds as follows:

$$^{2}_{1}H + ^{3}_{1}H = ^{4}_{2}He + ^{1}_{0}n + 17.59\ MeV$$

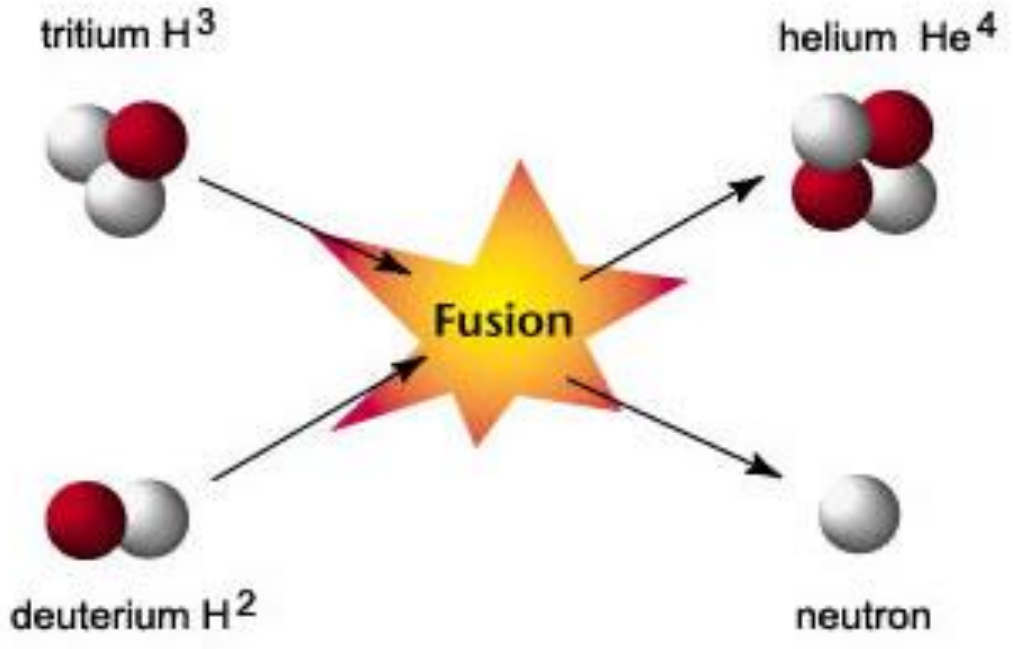


Fig.2.1 The nuclear fusion reaction.

This is the reaction between deuterium (D), and tritium (T) which on fusion yields an alpha particle (^4_2He) and a neutron and 17.59 MeV of energy[1] . The released energy is taken up by the two new particles; one fifth is taken up by the kinetic energy of the helium nucleus and four-fifths by the kinetic energy of the neutron. And the fast neutrons emitted are the primary means by which energy leaves the fusion reactor. These neutrons would leave the reactor on its outer edge and rest come in a component known as "Fusion Blanket". This blanket material is designed to slow down the fast neutrons and also to extract heat. This heat is transferred to a medium such as high-pressure helium or steam. And can be used to generate electricity by using turbine [2]. These blankets would contain lithium based ceramic materials which reacts with the fast neutrons to generate tritium, one of the two fuels required for the reaction [3].

For a good Fusion blanket a candidate material must exhibit good thermo physical, chemical, and mechanical stability at high temperature, be compatible with other blanket and structural materials, and possess desirable irradiation behavior, low electric conductivity, potentially high tritium generation and fast tritium release. Keeping these properties in mind, the ceramic materials fulfill several of these characteristics. They have been intensively investigated for the development of a fusion reactor the ceramic materials containing lithium are appropriate for tritium generation due to the nuclear reactions:[5]

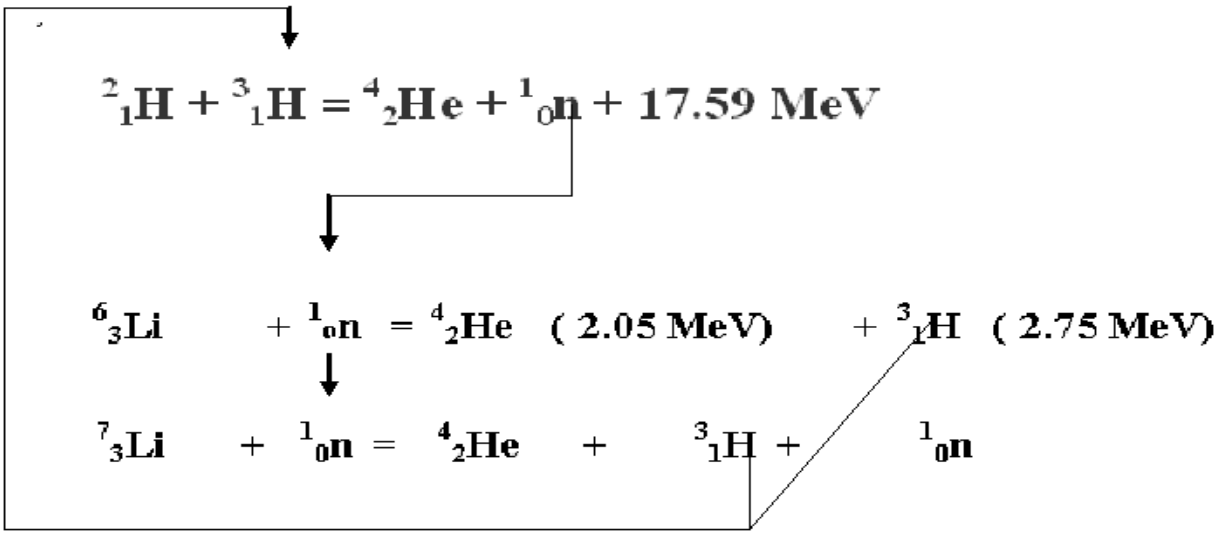


Fig. 2.2 In situ process tritium release by lithium atom.

Lithium is the only material suited for this task produces tritium by in situ.(Fig2.2) when irradiated with high energy neutron. Presently material like liquid lithium and its alloys and certain lithium containing solids, principally the lithium containing ceramics are used. So, another of the requirements is a high density of lithium atoms in their structure. Some proposed ceramic materials are Li_2O, $LiAlO_2$, Li4SiO4, Li_2ZrO_3, Li_2SnO_3 and more recently Li_2TiO_3 have gain more interest. Each one of these materials has their advantages and disadvantages that should be kept in mind before choosing a material to use. [4-6]

Different Lithium ceramic based material which is used in Fusion blanket module are Li_2O, $LiAlO_2$, Li_4SiO_4, Li_2ZrO_3, Li_2TiO_3.Among these Li_2TiO_3 are one of the best ceramic breeder material for the fusion blanket . Because Li_2TiO_3 have good thermal conductivity, high thermal stability, good chemical stability, and better mechanical property compared to other ceramics breeder materials.[9-11]

Fusion blanket can be made from pellets or from packed pebble bed , but the pebble give good features like, easy for making complex shapes blanket, uniform pore network, low sensitivity to irradiation damage and cracking, high average bed density and good purge gas drop. So pebble blanket is advantageous and the pebble developed from Li_2TiO_3 have good microstructural characteristics (open/closed) porosity, grain size, specific surface area, the fabrication process of Li_2TiO_3 pebble is easy and also we can vary the microstructural characteristics of the pebbles fabricated, so it is very advantageous to use Li_2TiO_3 for making pebble for the Fusion Blanket.[14-18]

Li_2TiO_3 powder can be synthesized through different techniques. Synthesizing techniques for Lithium titanate depend on cost as well as applications. Also the quality of the final powders is influenced by the synthesis rout. Li_2TiO_3 has been prepared by basically two techniques Solid state route, Chemical solution based route. In Solid state route techniques involves is mixing of precursors in their oxide or carbonate form, either by hand mixing or by high energy ball milling. And then calcination is done to get Li_2TiO_3 powder.[10,13,20]

For the synthesis of pebble; extrusion, spheronisation, sintering method is best for making the pebbles as it is appropriate one and fast method to obtained pebble desired. This process allows to obtain pebbles with high purity and fulfillment of the goal characteristics, the process is relatively simple and inexpensive, the process is flexible and can be adjusted to a range of pebbles specifications (pebble size, pebble density, pebble grain size). [15,25]

3. Literature Review:

Li_2TiO_3 are recognized as attractive tritium breeding material .Lot of work has been done on the fabrication of the Li_2TiO_3 ceramic powder, the sintering behavior, the tritium release behavior and other properties ,but the ceramic breeder researchers are now more oriented towards design aspect of breeder blanket ,and the pebble fabrication process and properties. [13] Preliminary research indicates that among Lithium based ceramics Li_2TiO_3 possessed attractive properties. Li_2TiO_3 has the same lithium density as that for $Li_2ZiO_3$and its melting point is similar. The thermal conductivity is better than that for lithium aluminate or lithium zirconates. Long-term waste problem should be low because titanium is the low activation element. Several conventional powder synthesis techniques including solid state synthesis, polymer solution technique, alkoxide route, sol-gel method, sol–gel process and indirect wet process are being followed by people.

Kleykamp et al [19]studied the phase diagram of Li_2O-TiO_2 system and found that binary Li_2O-TiO_2 system have mainly four ternary oxides: Li_4TiO_4, Li_2TiO_3, $Li_4Ti_5O_{12}$ and high temperature phase Li2Ti3O7 which decomposes eutectoid ally at 950^oC. The Li_2TiO_3 exists in three modifications, α, β and γ . The phase of Li_2TiO_3 is metastable and has a monotropic transformation to β phase at above 300_oC. This low-temperature β phase is monoclinic, and structure similar to Li_2SnO_3 type structure. The β to γ transformation takes place at 1155^oC. The γ phase has high temperature cubic phase and crystal structure similar to NaCl type.

Lang et al. has described Li_2TiO_3 is iso-structural with Li_2SnO_3, a derivative structure of sodium chloride. The cations Li and Ti are randomly distributed in the cation sites of rocksalt structure. It is proposed that in Li_2TiO_3 two types of layer structure exist; one composed of Lithium

occupied octahedra and the other composed of Lithium and Titanium occupied octahedra in 1:2 ratio stacked alternately perpendicular the ab plane. In Li_2TiO_3 all the octahedral edges are shared between two Ti, two Li, or one Ti and one Li and the O-O bond distances have different values which give the distortion in the rocksalt structure .

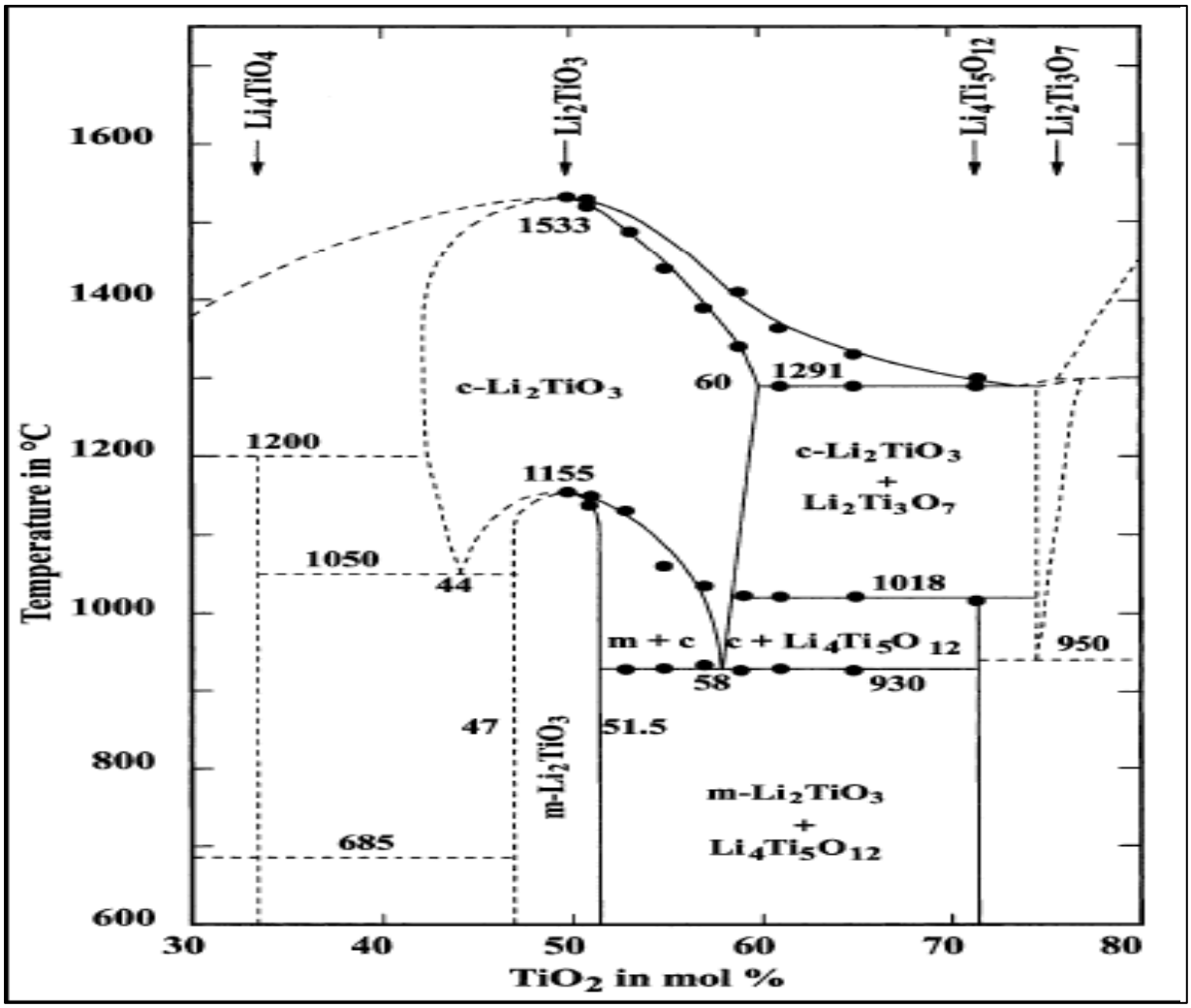


Fig. 3.1 Li_2O-TiO_2 phase diagram

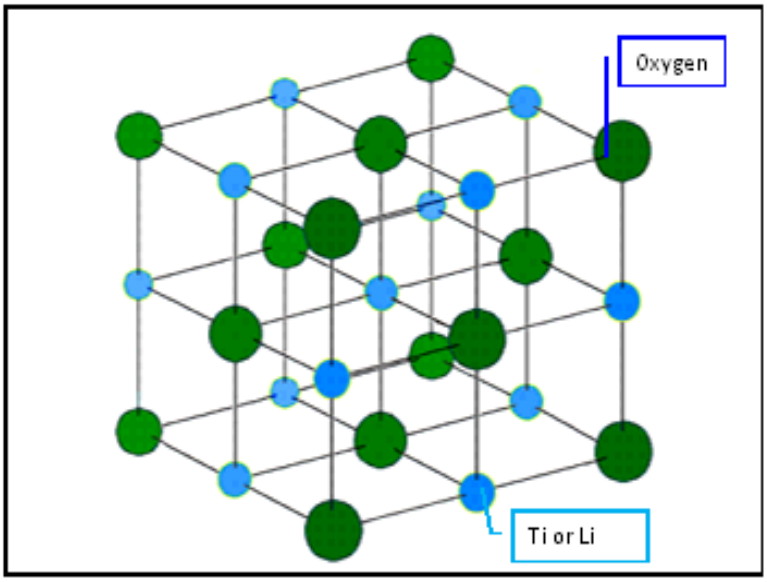


Fig: 3.2 Crystal Structure of Li_2TiO_3

Ceramic materials containing lithium are appropriate for tritium generation due to the nuclear reaction:

$$^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}He\ (2.05\ MeV) + {}^{3}_{1}H\ (2.75\ MeV)$$

Campos et. al. [21] studied tritium release behavior of Li_2TiO_3 by cluster model in the form of the $\mathbf{H_6TLiTi_6O_{12}^{+8}}$ **and** $\mathbf{H_{12}TLi_7O_{12}^{-4}}$ clusters and proposed that the occupation of tritium atoms in lithium titanate is realized preferably in octahedral sites near lithium layers followed by substitutional sites in lithium layers and titanium layers, respectively. Substitutional sites for tritium atoms in lithium layer have the biggest probability for release of tritium, considering that 75% of the lithium is in the lithium layers, the same ratio applies to the distribution of lithium vacancies and correspondingly to the substitutional tritium . Also the tritium released at lower temperature (330–450 ^{0}C) and 72–90% of the tritium was released in this temperature range (330–450 ^{0}C).

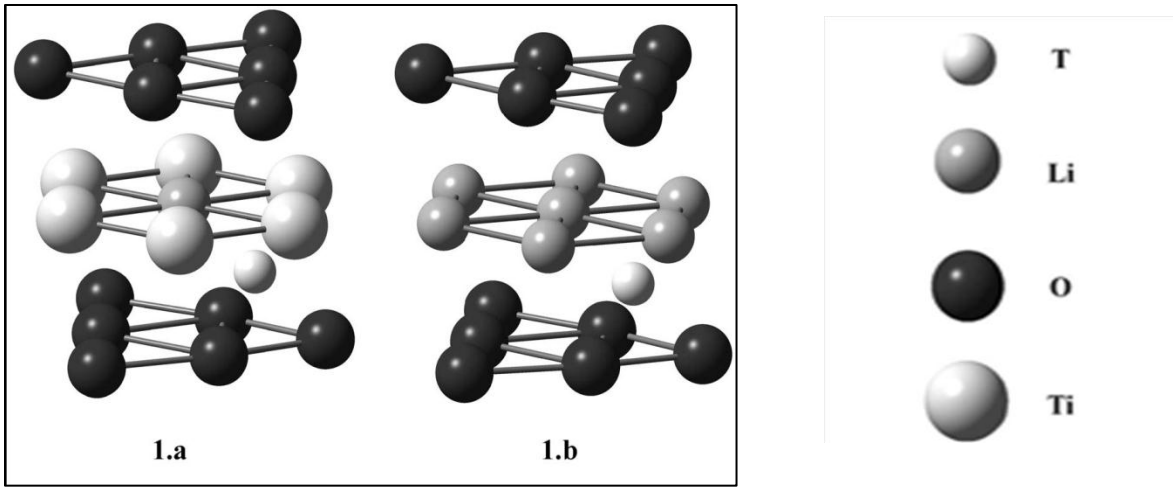


Fig.3.3 Cluster model for octahedral sites in Li_2TiO_3 (1.a) $H_6TLiTi_6O_{12}^{+8}$ (1.b) $H_{12}TLi_7O_{12}^{-4}$

Wu et.al. [17] in their work prepared the samples by solid state synthesis route taking Li_2CO_3 and TiO_2 powder in appropriate amounts corresponding to the Li/Ti atomic ratio of 2 in the final ceramic products were mixed by ball milling for 4 h with ethyl alcohol as the milling medium. Li_2TiO_3 powders were formed by calcining the dried powder at 700 ^{0}C for 4 h in air atmosphere. Calcination temperature is high because for solid state method diffusion of ionic species takes place through solid state for the product formation.

Roux et. al. [15] have studied the fabrication of Li_2TiO_3 pebble by extrusion spherodisation sintering process and for the experiment prepared the Li_2TiO_3 powder by solid state route and made pebbles of 1mm size ,found that this process allows to obtain pebbles with high purity for the fulfillment of the goal characteristics, the process is relatively simple and inexpensive, the process is flexible and can be adjusted to a range of pebbles specifications (pebble size,pebble density,pebble grain size). Major impurities in (ppm) level are Al, Ca, Cr, Fe, K, Ni,S ,Si ,Na, C . and the best performance was found for pebbles sintered at 1050 ^{o}C by performing test on these like; High-temperature long term behavior,Uniaxial compression tests and creep tests of Li_2TiO_3 pebble beds and Tritium release behavior.

4. Scope of Work:

From the literature review we observed that Li_2TiO_3 is a promising candidate's material for tritium breeding blanket for the D–T based fusion reactors because of its good lithium atom density, better tritium release and also good mechanical thermal chemical stability. Also the blanket made of spherical pebble give god properties like ; easy for making complex shapes blanket, uniform pore network, low sensitivity to irradiation damage and cracking, high average bed density and good purge gas drop. Solid state method is advantageous for preparation of Li_2TiO_3 powder in large scale which is required for pebble making by extrusion spheronisation technique. Effect of binder addition on final properties (e.g. density, thermal expansion coefficient) is also important for pebble fabrication, but there are very little information in public domain.

5. Objectives:

- To prepare phase pure Li_2TiO_3 powder by solid state synthesis route and its characterization by DSC /TGA, XRD, particle size analysis and to study the shrinkage behavior of green compact by dilatometer.
- To study the effects of binder content and sintering temperature on properties (bulk density, porosity, linear shrinkage, thermal expansion behavior) of Li_2TiO_3 pellets.
- To fabricate Li_2TiO_3 pebbles by Extruder-Spherodiser.

6. Materials and methods:

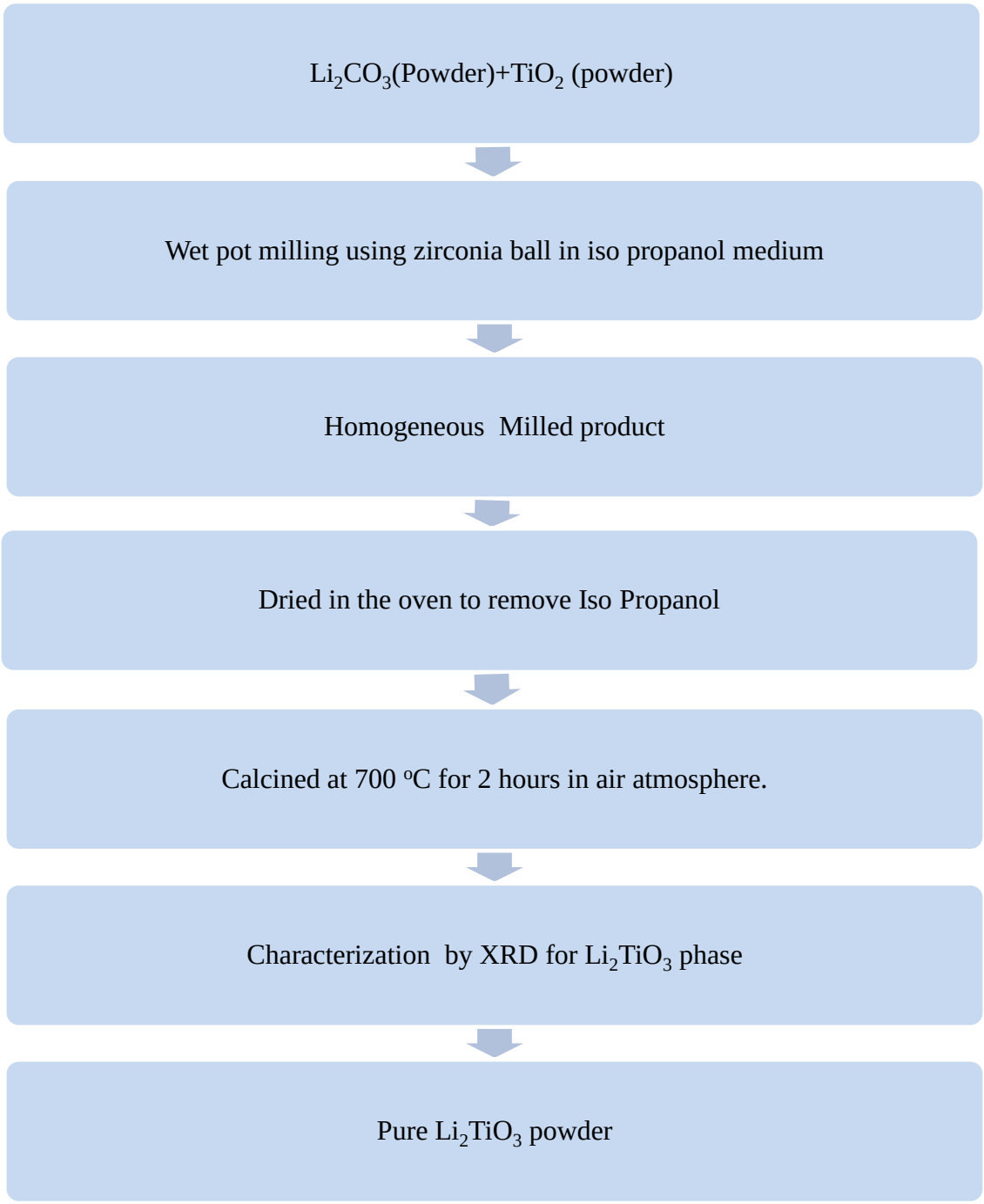
6.1 Raw Materials required:

- Li_2CO_3 powder
- TiO_2 powder
- Poly Vinyl Alcohol (PVA)

6.2 DSC /TGA of (Li_2CO_3 + TiO_2) mixed powder: (Li_2CO_3 + TiO_2) mixed powder is studied by scanning calorimeter (DSC) and thermo gravimetric analysis (TGA) using NETZSCH STA (Model No 409C) to know the decomposition behavior on calcination.

6.3 Li_2TiO_3 Powder preparation by solid state route synthesis: Solid state synthesis method was used to produce powder for the experiments. Li_2TiO_3 was prepared by wet milling of Titanium oxide (TiO_2) powder, Lithium carbonate (Li_2CO_3) powder using iso propanol medium. A batch of 20 gram is made for milling by mixing 14.5588 gm TiO_2 powder and 13.4658 gm Li_2CO_3 powder and then around 30 ml Iso propanol is added and total mass is mixed in pot mill using zirconia balls for 6 hours. Then milled product is dried and regrinded in agate motar to make it fine powder after then powder is kept in a alumina crucible and Calcined at 700 ^oC for 2 hours in air atmosphere in chamber furnace. After that the XRD analysis of the calcined powder is done by PHILIPS Diffractometer (model: PW-1830, Philips, Netherlands) using Cu Kα radiation XRD machine having Cu anode operating at 40 kv, in the $2Th^0$ (15^0-70^0) angle range. Raw data obtained from the XRD is analyzed by using X Pert High score Software to confirm the phase of Li_2TiO_3. Then we obtained pure Li_2TiO_3 powder. These pure powders are used in performing experiment in the thesis.

6.4 Preparation flow chart of Li_2TiO_3powder making:



6.5 Shrinkage Behavior of Li_2TiO_3 powder: Li_2TiO_3 powder is pressed to form a rectangular pellet and these pellets are fired in dilatometer to know the shrinkage behavior of powder.

6.6 Particle Size Analysis: To determine the particle size distribution of the powder laser diffraction method with a multiple scattering technique is used. A He-Ne laser is commonly used for the light source. The particles of Li_2TiO_3 powder was dispersed in water by horn type ultrasonic processor [Ultrasonic Processor Sonopros, PR1000 MP] and [ZETA Sizers Nano series (Malvern Instruments Nano ZS)] particle size analyzer is used to find out the particles size distribution.

6.7 Pellet Making: The Calcined pure Li_2TiO_3 powder was mixed with PVA solution (for binding). In three batches of 9 gram each with different amount of PVA varying from 3%-7%. It was then mixed in agate mortar and left for drying in open atmosphere. After drying it was grounded to fine powder. And 0.6 gram batch of mixed powder is weigh and then packed in separate packets .The powder is then pressed to form pellets by a load of 4 ton applied for 90 sec in cylindrical mold of 12.5 mm diameter. After that green weight of each pellet is measured.

6.8Sintering of green pellets: Pellets are sintered in chamber furnace in air atmosphere in the Temperature range of 900 ^oC – 1100 ^oC. Weight of each pellets are measured after firing.

6.9 Bulk Density measurement: Bulk density (BD)of each pellets is measured by using BURP(boiling under reduced pressure) apparatus in which pellets are boiled in kerosene for 1 hour and then its bulk density is measured by measuring ,Dry weight(D), soaked weight(W) and Suspended weight(S),using formula:

BD= D/(W-S) and apparent porosity (AP)= (D-W)/(W-S)

As we know theoretical Density of Li_2TiO_3 is 3.43

So, %Density of pellets= (BD/3.43)*100

6.10 Phase Analysis of sintered pellets: XRD of each pellets are done by XRD Philip`s Diffractometer (model: PW-1830, Philips, Netherlands) using Cu Kα radiation machine operating at 40 kv, in the $2Th^0$ (15^0-70^0) angle range and XRD data is analyzed and studied by using X Pert High Score Software.

6.11 Thermal expansion Behavior analysis by using Dilatometer: Thermal expansion behavior of each sintered pellets are done by heating pellets at 10 ^{0}C higher than sintering temperatures at a heating rate of 10 ^{0}C/ min. in dilatometer.

6.12 Microstructural analysis using SEM: To study the microstructure of pellets SEM analysis is done in which JEOL JSM-6480 SEM instrument was used. The pellets were sawn from the center by diamond blade and the surface obtained is polished and thermal etching is done at a temperature 100 ^{0}C less than sintering temparture. After that platinum coating is done at 20 mA for 3 minutes by using JEOL JFC- 1600 fine coater. Picture obtained at different resolution are used to study microstructural property.

6.13 Pebble making and its density measurement: Spherical pebble is made by Using UICE Lab Machine a integrated Extruder Spherodiser machine which produce spherical pebble from wet mass which has a capacity of 50 gram to 100 gram per lot of charge fed. LI_2TiO_3 pebble is made by mixing 50 gram Li_2TiO_3 powder with binder in a agate motar for 15 minutes and then whole mixture is fed into Extruder which is rotating at 90 rpm and then we obtained vermicelli from 1.2mm sieve ,these vermicelli are then fed into Spherodizer chamber in which chequered plate is rotating at 900 rpm its rotation is varied from 900 to 1700 rpm during the process fro few minutes and then spherical pebble is obtained which is dried at 100 ^{0}C after that these pebble are sintered at 900 ^{0}C,1000 ^{0}C,1100 ^{0}C .

6.14 Density of pebbles: Pebble density is measured using pycnometer.by measuring; weight of bottle (W1), weight of bottle with pebble (W2), Weight of bottle with kerosene and pebble (W3) and weight of bottle with kerosene. After calculating all these True Density (TD) of pebble is given by:

TD= (W2-W1)/{(W4-W1)-(W3-W2)}*0.81

%Density = TD/3.43

7. Results and Discussions:

7.1 DSC/TGA analysis.

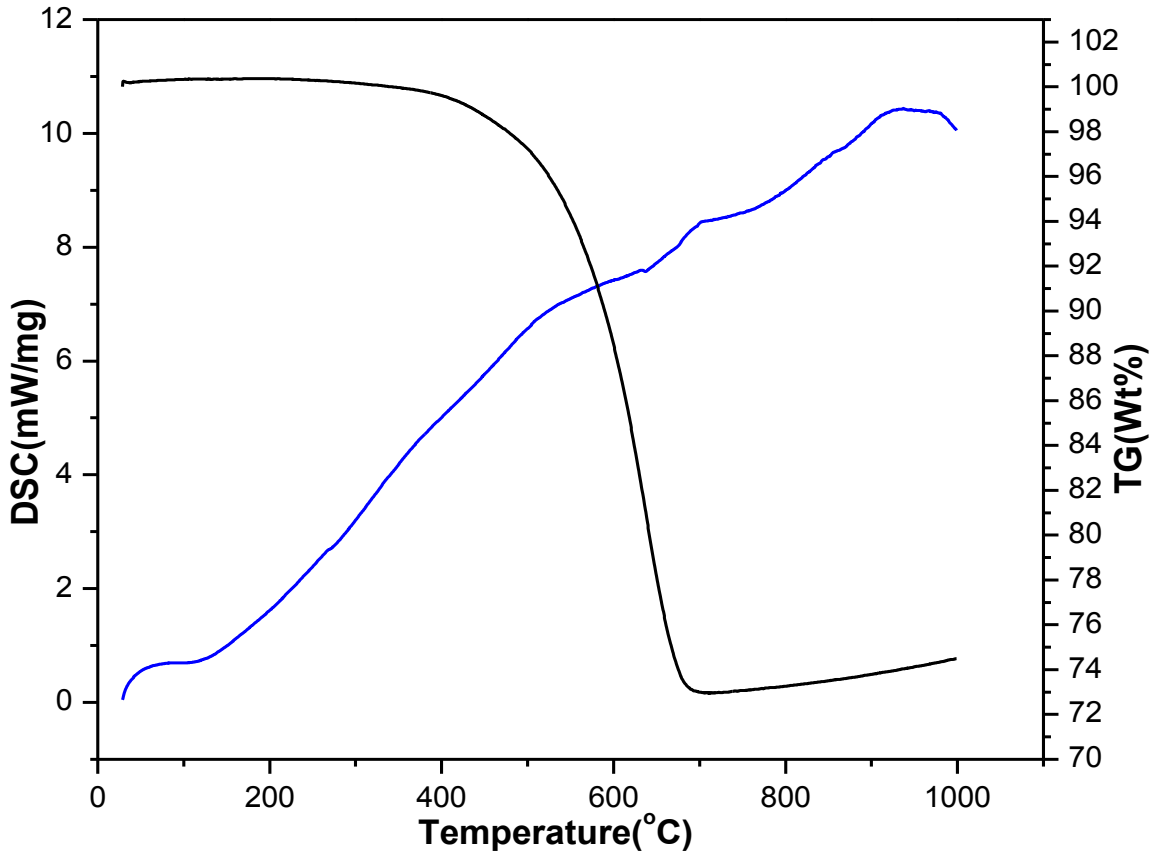


Fig. 7.1 DSC /TGA of (Li_2CO_3 + TiO_2) mixed powder.

Fig7.1 DSC/TGA of the stoichiometric mixture of Li_2CO_3 and TiO_2 raw powder shows that weight loss started around 500^oC and completed at 700^oC. The weight loss may be due to decomposition and reaction between Li_2CO_3 and TiO_2. Exothermic peak at 700^oC corresponds to crystallization of Li_2TiO_3 phase.

7.2 Thermal Shrinkage analysis.

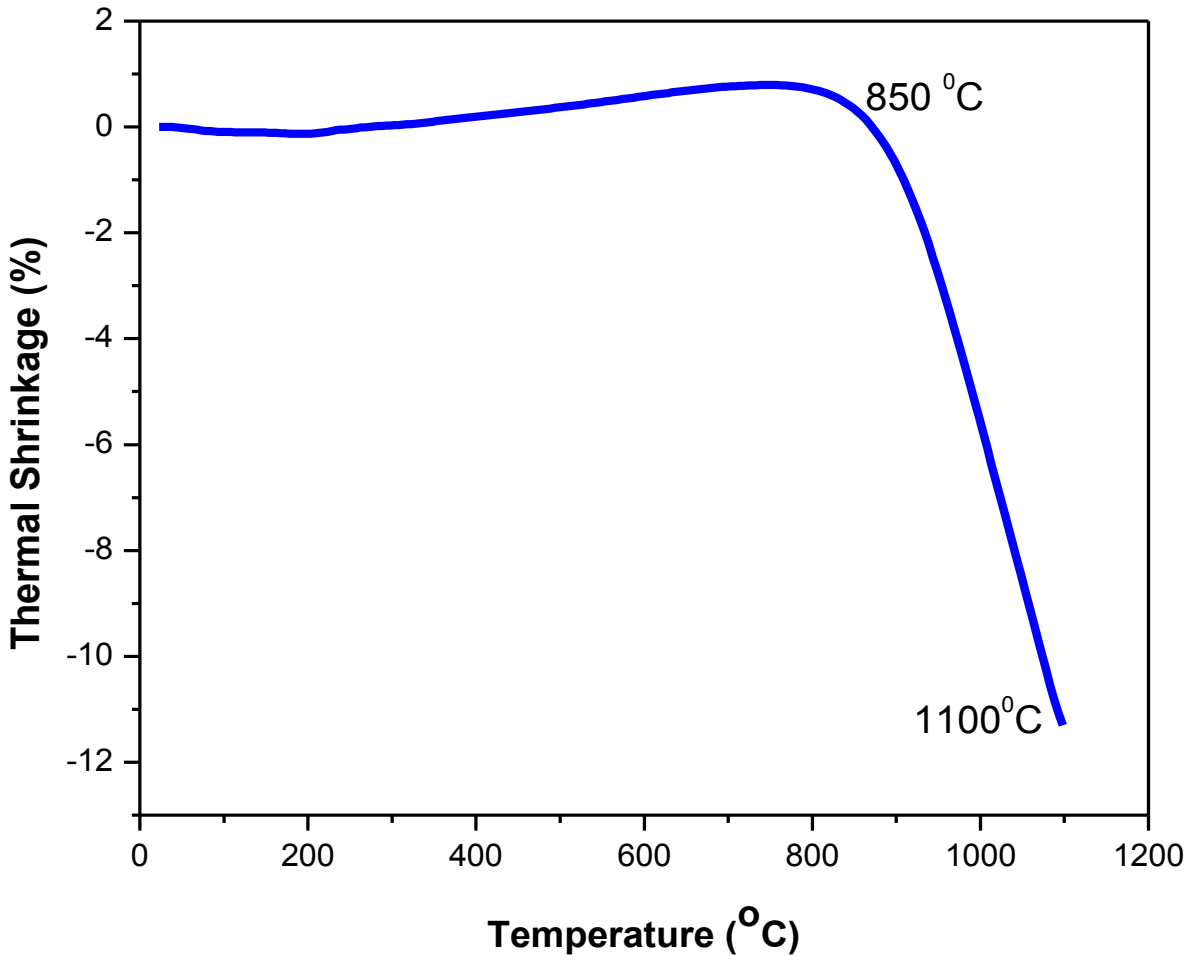


Fig.7.2 Shrinkage behavior of Li_2TiO_3 powder compact.

Fig.7.2 shows the shrinkage behavior of Li_2TiO_3 powder compact with temperatures. It is clear from the figure that shrinkage starts around 850^0C and almost completed at 1100^0C. Shrinkage is around 11% in this temperature range. Powder compact was sintered at three temperatures 900^0C, 1000^0C and 1100^0C for further study.

7.3 XRD analysis of Li_2TiO_3 powder.

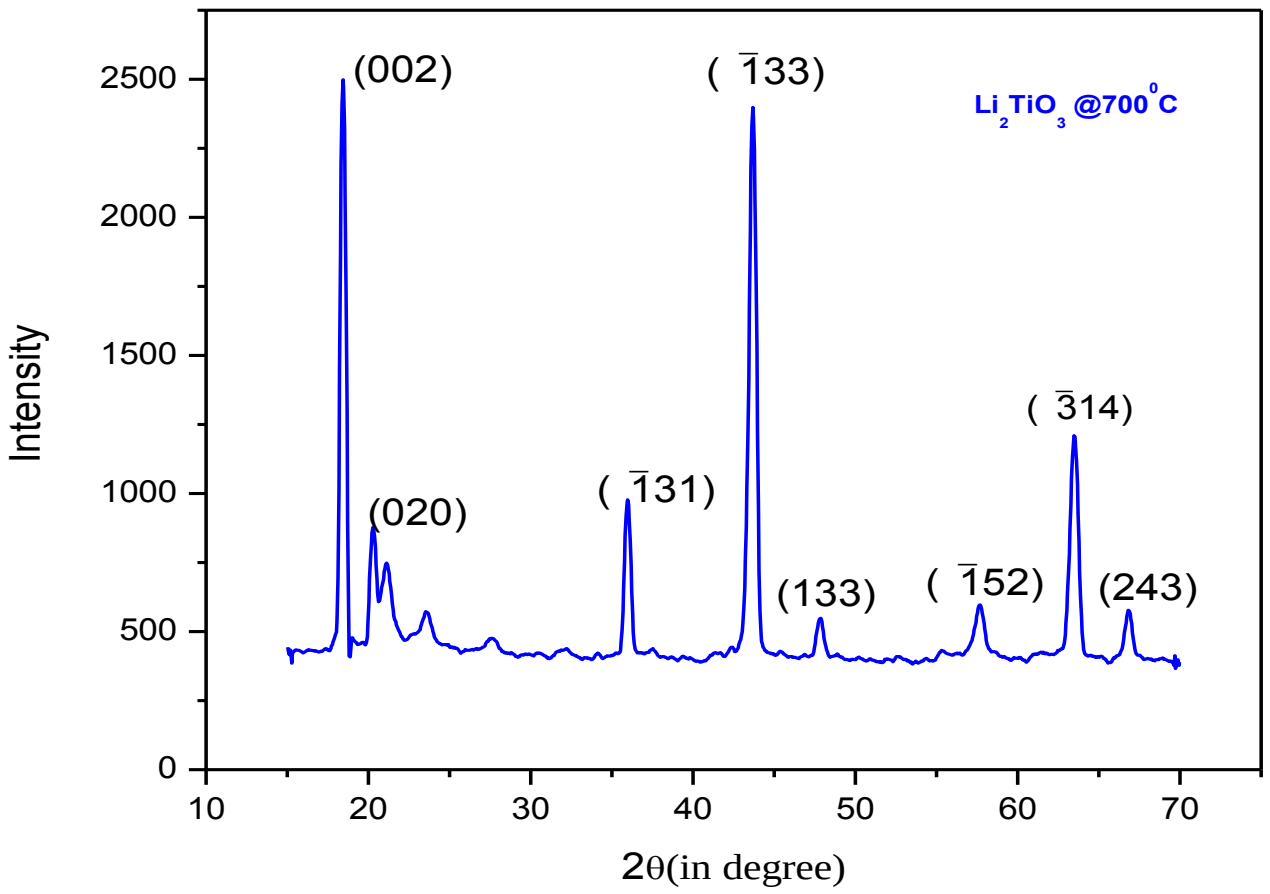


Fig. 7.3 XRD of the pure Li_2TiO_3 powder calcined at 700 ^oC.

Fig 7.3 XRD graph of Li_2TiO_3 analyzed by X Pert High Score software confirms that all peaks are matched with Li_2TiO_3 phase (JCPDS file 00-033-0831)

7.4 Particle Size Analysis

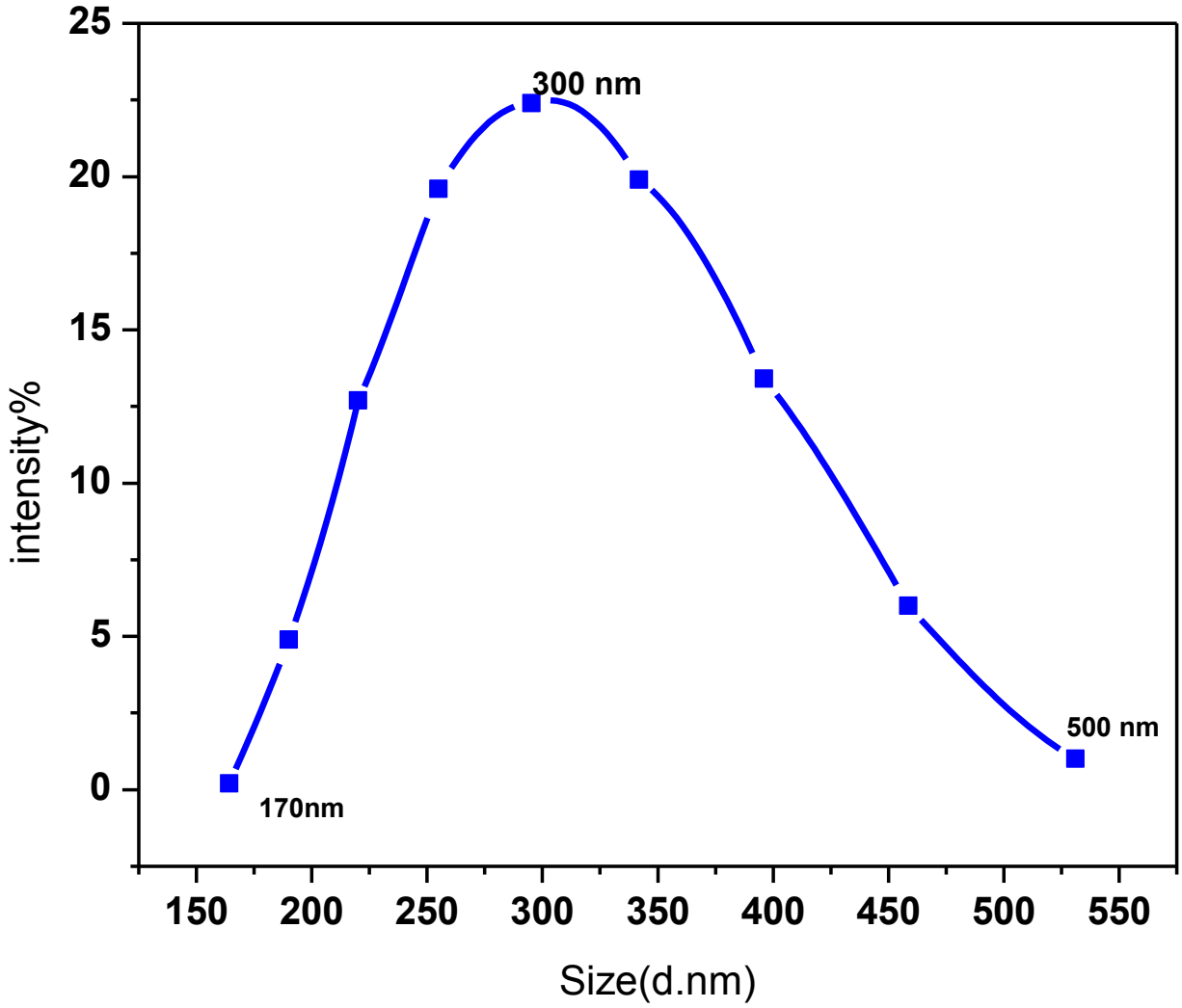


Fig. 7.4 Particle size distribution of Li_2TiO_3 powder

Fig.7.4 shows that particle size is in the range of 170-500 nm. Ultimate goal is to fabricate spherical pebbles of Li_2TiO_3. For pebble fabrication it may require higher binder content than pellet preparation. So here three different PVA (binder) content (e.g. 3, 5, 7 wt%) was used to prepare pellets for sintering.

7.5 Density analysis of sintered pellets:

Table for Density measurement of pellets sample						
%PVA	**Sintering Temp.^{0}C**	**GreenWt.(gm)**	**Wt.(gm)Sintered)**	**Bulk Density**	**%Density**	**Average Density**
3	1100	0.6165	0.5783	3.275685	95.50103	95.48881
3	1100	0.6228	0.5846	3.256713	94.94789	
3	1100	0.6291	0.5859	3.293400	96.0175	
5	1100	0.5480	0.5072	3.257986	94.98501	95.39926
5	1100	0.6159	0.5758	3.275267	95.48883	
5	1100	0.6069	0.5683	3.283331	95.72393	
7	1100	0.6078	0.5713	3.165205	92.28003	92.49999
7	1100	0.7487	0.7043	3.178178	92.65826	
7	1100	0.6070	0.5703	3.174866	92.56169	
3	1000	0.6142	0.5789	3.272219	95.39997	95.75781
3	1000	0.6237	0.5841	3.290132	95.92222	
3	1000	0.6076	0.5729	3.291128	95.95124	
5	1000	0.6110	0.5723	3.285351	95.78282	95.63988
5	1000	0.6107	0.5701	3.293730	96.02712	
5	1000	0.6105	0.5715	3.262262	95.10968	
7	1000	0.6094	0.5739	3.271351	95.37467	94.73332
7	1000	0.6087	0.5729	3.227045	94.08293	
7	1000	0.6066	0.5717	3.249663	94.74237	
3	900	0.6030	0.5810	3.026431	88.23414	88.08744
3	900	0.6040	0.5808	3.041034	88.65989	
3	900	0.5890	0.5605	2.996733	87.3683	
5	900	0.5912	0.5731	3.012401	87.8251	87.58303
5	900	0.6063	0.5738	3.012171	87.8184	
5	900	0.5910	0.5732	2.987722	87.1056	
7	900	0.6050	0.5739	2.972244	86.65435	85.97044
7	900	0.6067	0.5735	2.932670	85.5006	
7	900	0.6059	0.5734	2.941444	85.75638	

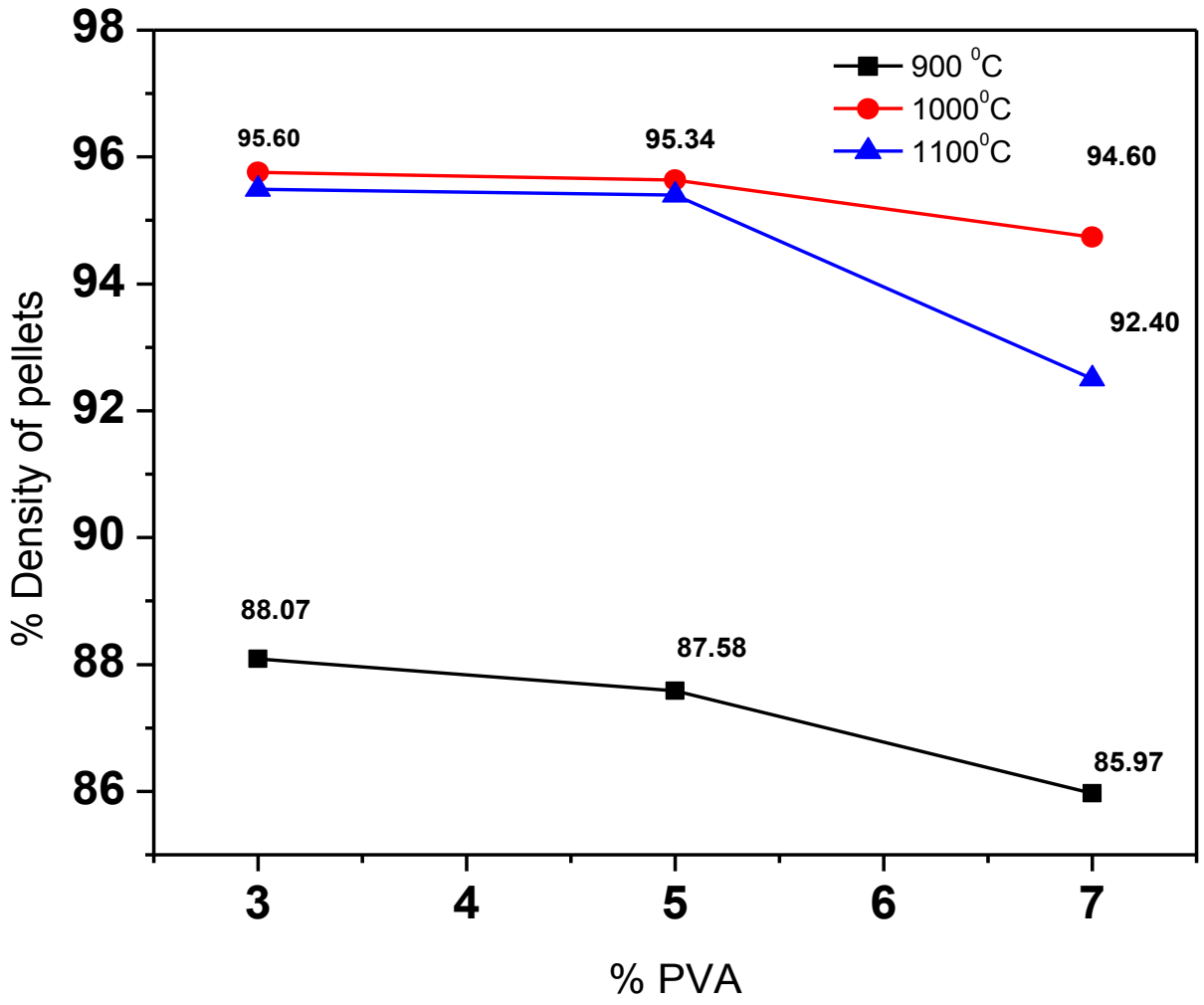


Fig. 7.5 Variation of density with different binder content at three different sintering temperatures.

Fig.7.5 shows that highest density (95.6%) is achieved with 3wt %PVA content when sintered at 1000 ^{0}C. Density of Li_2TiO_3 pellets decreases with increase in binder content from 3wt% to 7wt%. The reason may be due to that higher amount of binder left significant amount of porosity during binder burnout which reduces the density of the samples. Density of Li_2TiO_3 increases with higher sintering temperature but slightly decreases at 1100^{o}C. Very high sintering temperature (1100^{o}C) promotes Li evaporation and creates closed porosity that may be the reason for fall in sintering density at higher temperature.

7.6: XRD analysis of sintered pellets.

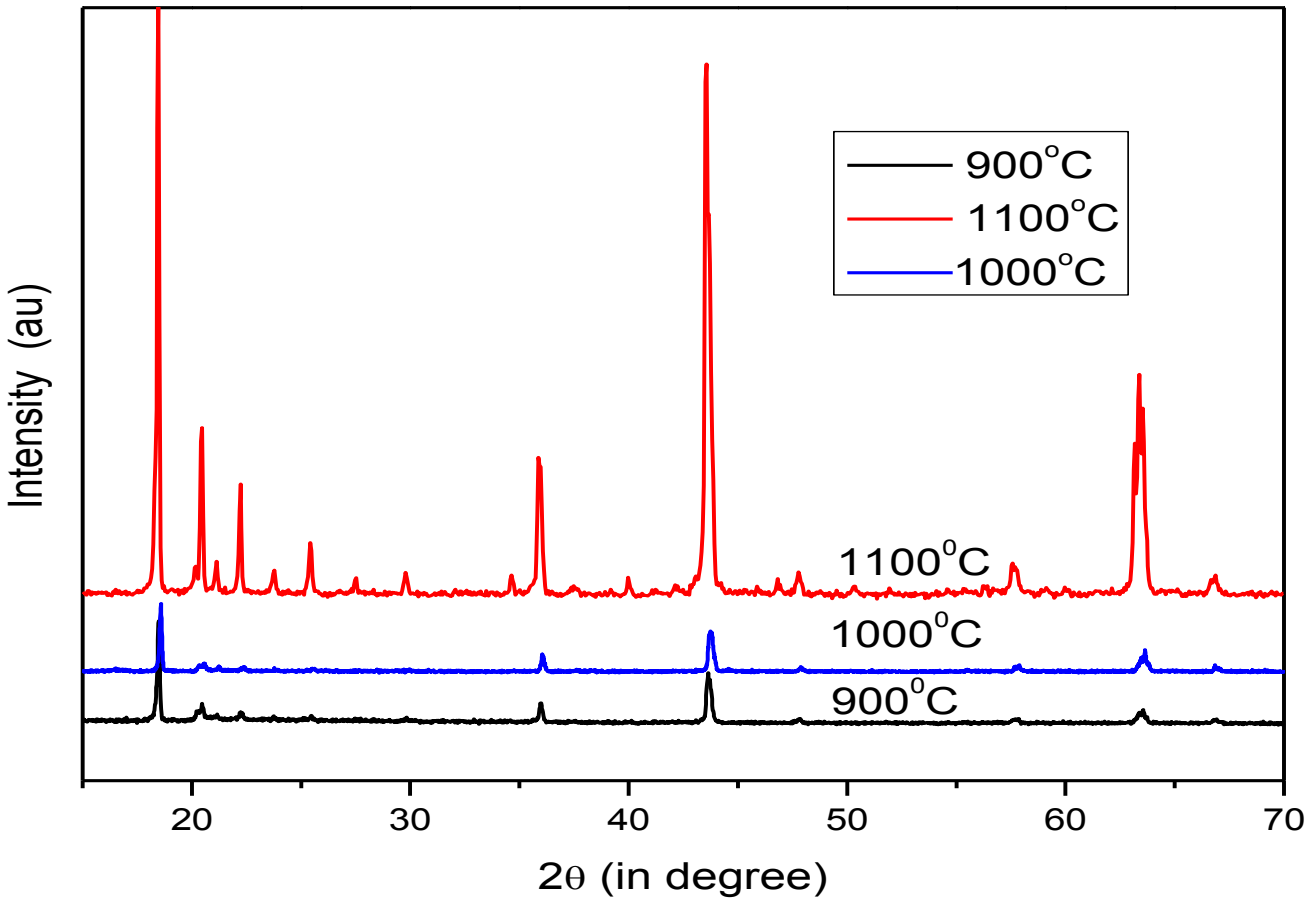


Fig7.6 XRD of Sintered Pellets densified at three different temperature.

Fig.7.6 is the comparative XRD graph obtained , on analysis by X Pert High Score software confirms that majority peaks matching with Li_2TiO_3 phase(JCPDS file 00-033-0831) and also shows that with increase in temperature peak get bigger in size also small peaks gets clearly visible at 1100 ^{0}C.

7.7: Thermal Expansion

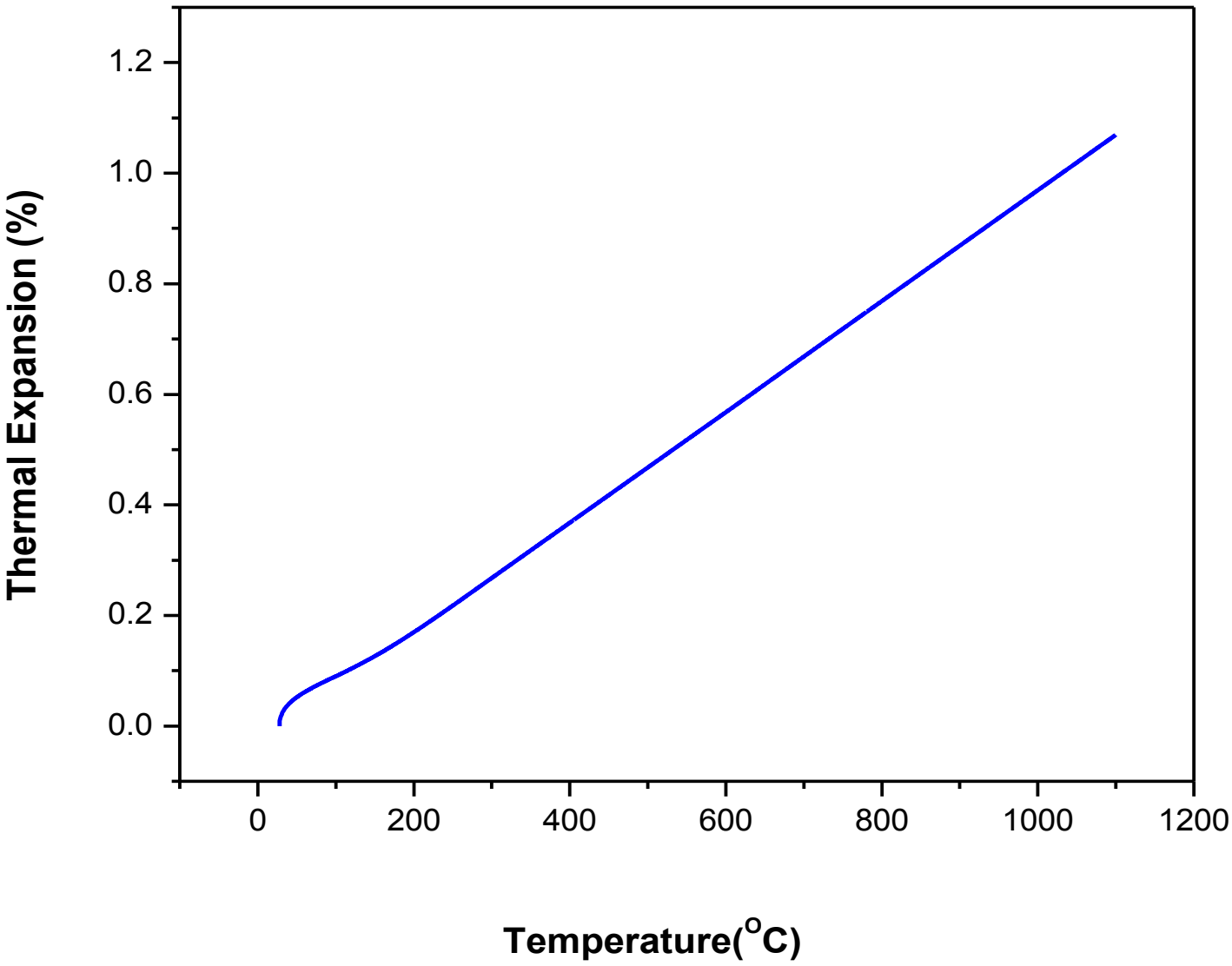


Fig. 7.7 Variation of percent thermal expansion with temperature for Li_2TiO_3 which shows 0.45% expansion at 500°C.

Table for Thermal Expansion Coefficient		
%PVA	Temp.	Thermal Expansion coefficent.@500 ^{0}C
3	900	17.266
5	900	17.256
7	900	17.10541
3	1000	18.198
5	1000	18.17096
7	1000	18.0086
3	1100	18.717
5	1100	18.743
7	1100	18.657

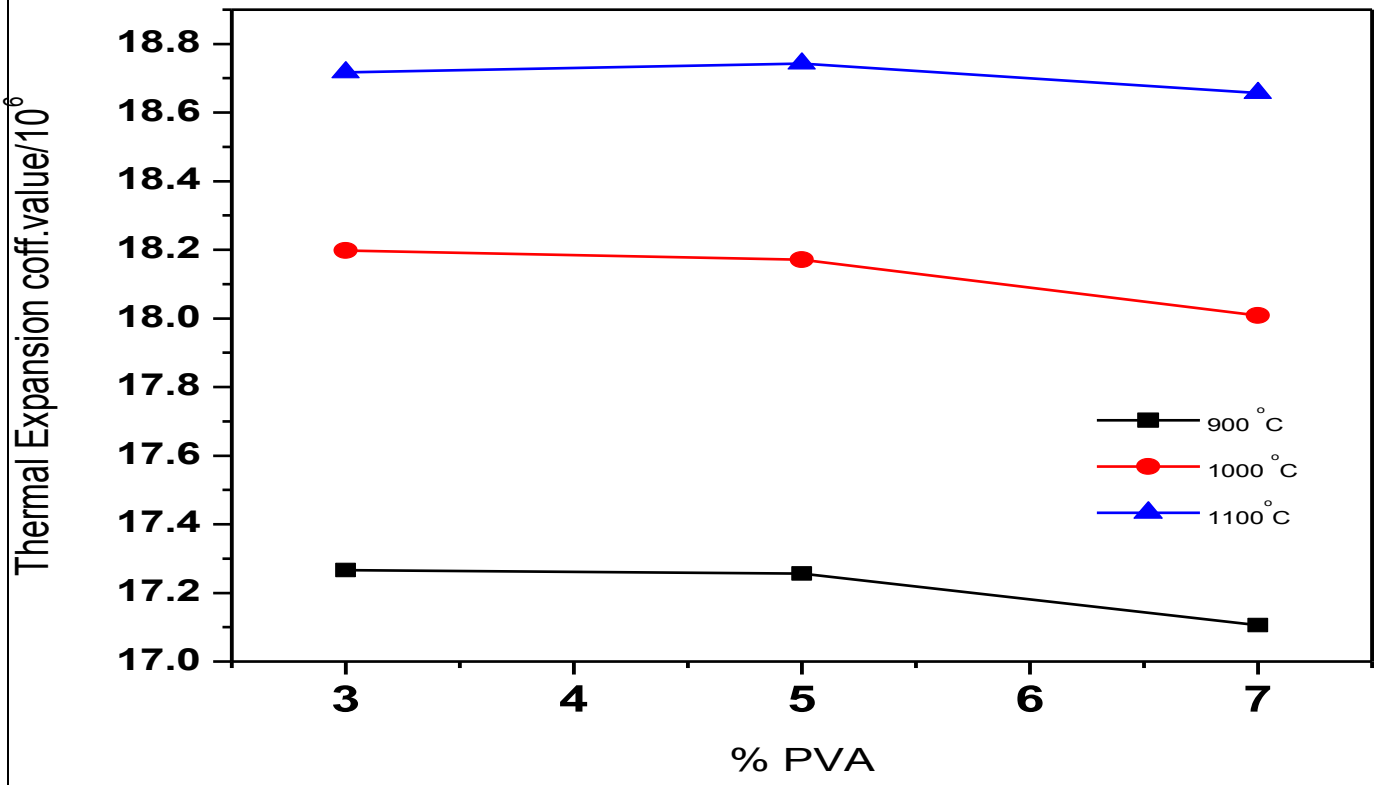


Fig 7.8: Variation of thermal expansion coefficient with %PVA at three different sintering temperatures

Fig 7.8 shows that Thermal Expansion coefficient value increases marginally (17.2×10^{-6} – 18.7×10^{-6}/oC) with increase in sintering temperature and it decreases with increase in binder content. Details microstructure analysis for all the samples are required to understand the behavior properly.

7.8 Microstructural analysis by SEM.

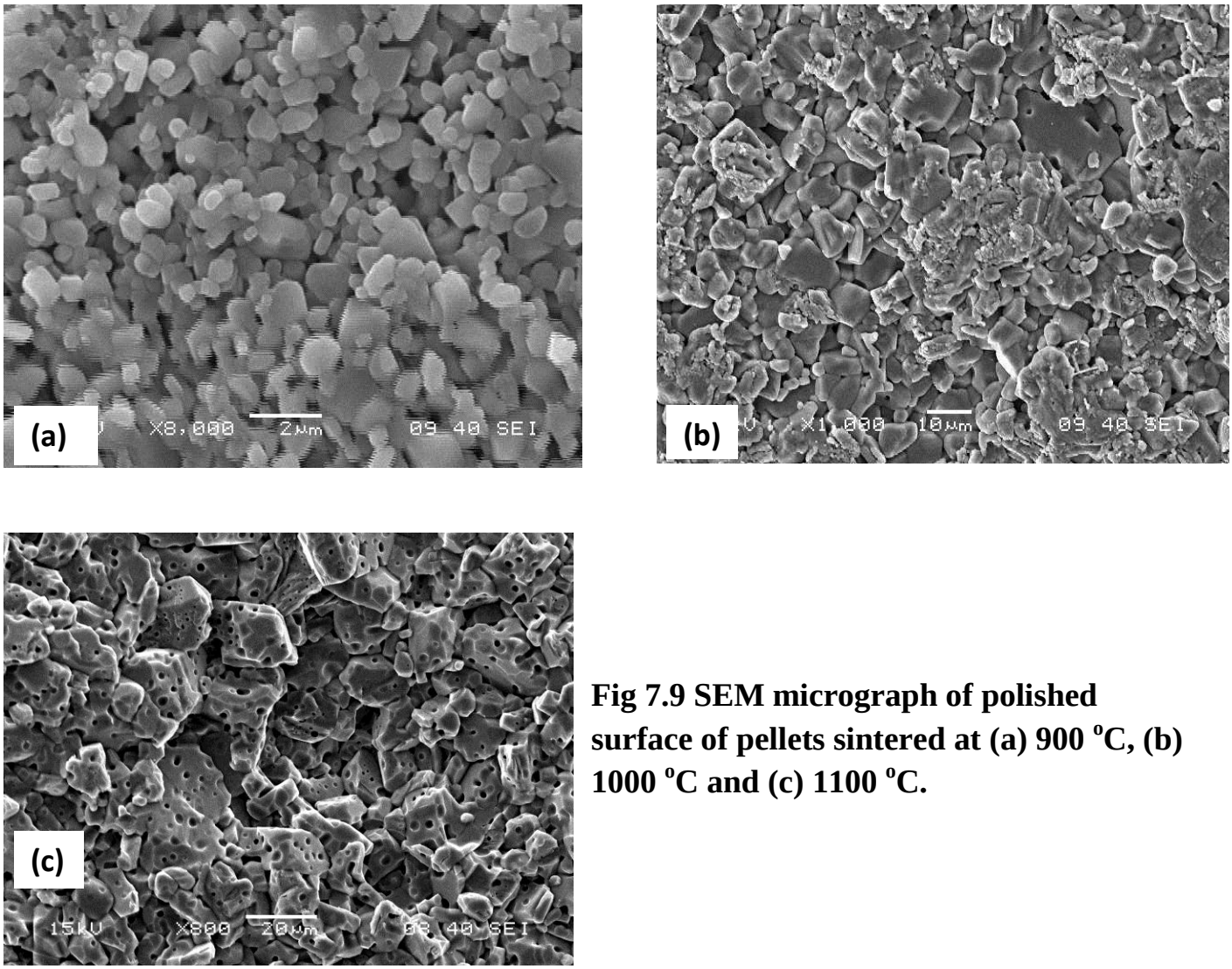


Fig 7.9 SEM micrograph of polished surface of pellets sintered at (a) 900 ^{o}C, (b) 1000 ^{o}C and (c) 1100 ^{o}C.

Fig.7.9 shows the microstructure of Li2TiO3 sample sintered at three different temperatures with 3 wt% PVA content. It is observed that lower sintering temperature (900 ^{0}C) produces small grain size which is varying from 1 to 2 µm. Higher sintering temperature produces grain growth. For 1100^{0}C sintered sample shows huge amount of close pore inside the grain.

7.9 Fabrication of pebbles:

Pebble form is preferred in fusion reactor. After exploring the effect of binder addition, 3 wt% PVA was used to fabricate pebble by extrusion spheronisation process. It is observed from the Fig.7.10 that with increasing sintering temperature density of the pebble improving but it is lower than the density of the pellet sintered at same temperature. Fig.7.11 and Fig.7.12 shows the photograph of green pebble and sintered pebble respectively. Diameter of the pebble varying from 1-3 mm. Further studies (optimization of extruder screw speed, binder and moisture content in powder, spherodiser rpm etc.) are required to get equal size and shape pebble.

Table for Density of pebbles			
%PVA	Sintering Temprature in ^{0}c	Bulk Density	%True Density
3	900	2.901923	84.60417
3	1000	2.995676	87.3375
3	1100	3.049112	88.89539

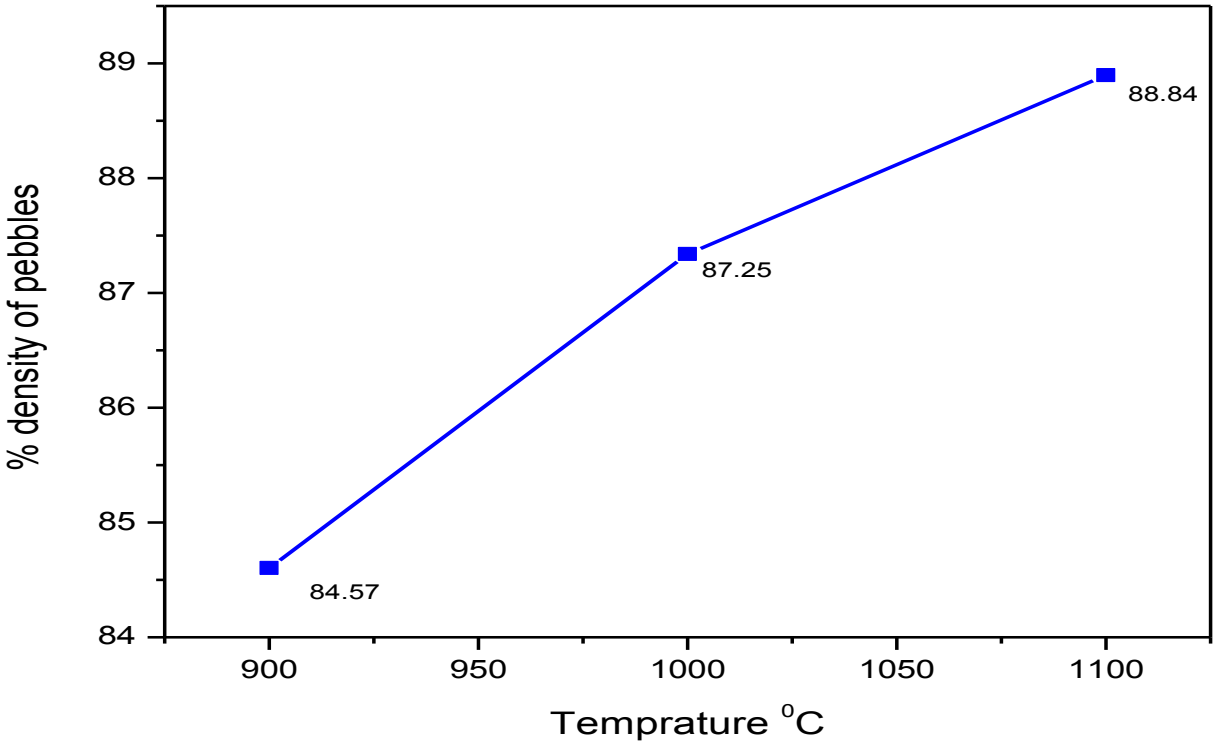


Fig 7.10 Variation of density of pebble with sintering temperature.

Fig 7.11 Green pebbles fabricated by extruder spherodizer

Fig7.12 Pebbles after sintering at 900oC with 3 wt% PVA content, diameter vary from1.5mm to 3mm

8. Conclusions:

- Phase pure Li_2TiO_3 can be prepared at 700^oC.
- Particle Size of the synthesized powder ranges from 200 -500 nm.
- Shrinkage behavior of Li_2TiO_3 powder shows that densification starts at around 850^oC and samples can be sintered to 88% of theoretical density at 900 ^0C. Highest density (95%) is achieved at 1000 ^0C with 3% PVA. Sintered density deteriorated with increase in binder content.
- Grain size of the sintered sample is strongly depends on sintering temperature. Higher sintering temperature (>1000oC) produces large grain size and closed porosity.
- Thermal expansion coefficient of the sintered sample ranges from (17×10^{-6} - 18×10^{-6} /^oC) and it decreases with increase in binder content.
- Optimization of binder content is very important factor during pebble fabrication. Lower amount of binder generates irregular shape and high amount of binder causes agglomeration of small green pebble to form bigger size pebble and sometime cause blockage of extruder.

9. Future work:

- We can study the effect of particle size by solid state route on pellets and pebble property.
- Comparison by Other routes of powder processing can be used to study the pebble property.
- Optimization of other processing parameters (extrusion speed, cheaqer plate speed etc.) of pebble making.
- Microstructural properties can be studied by SEM.
- Other pebble properties also need to be studied, like strength, Impurity analysis.

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